



A Study on Nitrate Ion Reduction in Water with Zero-Valent Iron Loaded Nano-Titania Prepared from Ilmenite Ore

M.H.H.MAHMOUD^{1,2,*}

¹Materials Science & Engineering Group, Chemistry Department,
College of Science, Taif University, Taif, Kingdom of Saudi Arabia.

² Central Metallurgical Research and Development Institute, P.O.Box, 87,
Helwan, Cairo, Egypt.

*Corresponding author E-mail : mheshamm@gmail.com

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ABSTRACT

This paper aims to synthesize titanium dioxide loaded with nano-zero valent iron (nZVI-TiO₂) from an inexpensive ilmenite ore. Ilmenite leachant, a solution rich in both titanium and iron ions, has been prepared by leaching ilmenite ore in hydrochloric acid. At 30% HCl, 70°C and 5 hours, almost all of iron and titanium in the ilmenite ore were dissolved. Nano titania was then produced by hydrolysis of the Ilmenite leachant in boiling water under open atmosphere and nano-zero valent iron (nZVI) was subsequently precipitated on its surface by reduction with sodium borohydride. The synthesized nZVI-TiO₂ was characterized by TEM, UV-Vis absorption, XRD and EDXRF and tested for reduction of nitrate ion from water. The synthesized material showed good performance in reduction of nitrate ion in water compared with nZVI. About 40% of nitrate ion could be removed using nZVI-TiO₂ from nearly neutral water after 3 hours.

Keywords: Nitrate ion, Reduction, Nano- Zero valent Iron, Ilmenite ore.

INTRODUCTION

Nitrate ion are considered as hazardous environmental contaminants of ground and surface water. According to the US Environmental Protection Agency (EPA), nitrate ion threshold concentration in drinking water should not exceed 10 mg/ Lit¹. However, this threshold level is surpassed in many cases due to many reasons, the most important being due to the intensive and uncontrolled use

of fertilizers in agriculture². Unfortunately, nitrate ions may persist for decades in groundwater and accumulate to high levels as more nitrogen based fertilizers are fed to the soil each year³. Various techniques have been adopted so far for drinking water denitrification: ion-exchange, reverse osmosis, adsorption, biological denitrification and chemical reduction⁴⁻⁶. These techniques have their advantages and disadvantages. Ion exchange and reverse osmosis suffer from a medium to high

operating cost due to the frequent regeneration of the media and production of secondary brine waste. Adsorption by ion exchangers suffers from strong pH and temperature dependency and spent adsorbent disposal problem⁷. Biological denitrification has a lower operating cost and is the prevalent method used for the moment. It suffers from excessive biomass and soluble microbial by-products. In addition, this process is relatively slow and, compared to the chemical reduction method, sometimes suffer from incomplete removal of nitrate ion⁸.

Nano sized zero valent metals possess a high specific surface area and a high surface reactivity. A technical problem associated with the industrial application of such materials is that they cannot be used alone and should be supported. Pillared clays and zeolites have been recently used as low cost effective supports for nano-scale zero valent iron⁹. Nano-sized support materials for zero valent iron can help in increasing the surface area without agglomeration. Nano titania is suggested to be a suitable support due to its high chemical stability at different aqueous media. In this work, ilmenite ore has been used to prepare nano-titania.

Natural ilmenite is an inexpensive raw material contains varieties of components such as TiO_2 , FeO , Fe_2O_3 and SiO_2 . The extraction methods of titanium from ilmenite can be summarized into two categories; pyrometallurgical and hydrometallurgical routes. Hydrochloric acid leaching is much simpler and the residual acid can be recycled to the process¹³⁻¹⁶. The titanium acidic solution should be further purified and hydrolyzed to produce pure TiO_2 ¹⁴.

We have previously utilized an Egyptian ilmenite ore for preparation of nano-titania by acid leaching, purification for separation of iron and hydrolysis. The prepared material was used as a catalyst loaded with different metal ions for removal of varieties of pollutants in water^{15, 16}.

Since zero-valent iron ($\text{Fe}(0)$) was first acknowledged as a treatment medium for environmental remediation nearly two decades ago¹⁷, it has been advanced into a viable and attractive option for treatment of many types of organic and inorganic contaminants¹⁸. Removal of contaminants

by $\text{Fe}(0)$ occurs via several physicochemical processes including chemical reduction, specific and nonspecific adsorption and coprecipitation. Ryu et al.¹⁹ demonstrated the utility of nano zero valent (nZVI) iron for nitrate ion reduction, highlighting the potential effect of particle aggregation and catalyst. Given the various limitations of $\text{Fe}(0)$ -based treatment systems, the successful removal of contaminants primarily depends on how well the reactivity of $\text{Fe}(0)$ can be sustained for a longer period of time. Sustained reactivity of $\text{Fe}(0)$ can be maintained by compensating hydrogen ions consumed during the reaction or by minimizing surface passivation by iron corrosion products. Numerous efforts to enhance performance of $\text{Fe}(0)$ have been made in recent years, with the most involving amendment of various additive materials into $\text{Fe}(0)$ reactions²⁰.

This work aims to present a new material for the chemical reduction of nitrate ion using an ilmenite ore for preparation of nano-titanium dioxide to be used as a support for the nZVI. Leaching of ilmenite in hydrochloric acid produced solution rich in both titanium and iron ions. The effects of conditions of titanium dissolution from natural ilmenite and hydrolysis were systematically studied. Thus, nZVI prepared by subsequent reduction of iron ions in the same solution. This is to promote the performance and stability of zero valent iron in reduction of nitrate ion by supporting it on nano titania. In this way, the prepared material benefits from enhanced chemical reactivity by keeping the iron particles without agglomeration. The effect of different loadings of zero valent Fe, solution initial pH and time on the nitrate ion anion removal were investigated.

EXPERIMENTAL

Materials and Instruments

A representative sample of 10 kg ilmenite ore from Abu Ghalaga region, Red Sea, Egypt, was thoroughly mixed, crushed and ground to 100% -200. The chemical analysis of the ilmenite sample, was determined using X-ray fluorescence (XRF), and was given in Table 1. Chemicals of analytical grade were used for the extraction and synthesis (hydrochloric acid HCl 37% Sigma Aldrich, sulfuric acid 98% Sigma Aldrich, sodium borohydride NaBH_4 (BDH), ethanol 99% Sigma Aldrich, NaOH 99%, NaNO_3 99%. Nitrate ion reagent was obtained from

Hack company (USA) and used for determination of nitrate ion by spectrophotometer DR6000, Hack (USA). Double distilled water was used during the whole work.

Chemical analysis of the ore was carried out by X-ray fluorescence (XRF) using Quant'xEnergy Dispersive-XRF Spectrometer. Chemical analysis of Fe ions in aqueous solutions was carried out using Atomic Absorption Spectrometer Model Perken-Elmer 3100. Titanium was determined spectrophotometrically by the hydrogen peroxide method at wavelength 410 nm²⁴. X-ray diffraction (XRD) patterns was obtained using an automated

diffractometer(Philips type: PW1840), at a step size of 0.02°, scanning rate of 2° in 2θ/min, and a 2θ range from 4° to 80°. Semi-quantitative phase analysis was performed applying X'PertHighScore Plus software.

Leaching of Ilmenite Ore

For studying the different parameters affecting the dissolution of titanium and iron from ilmenite, small scale experiments were firstly applied. A 20 g ilmenite ore was inserted into a Pyrex flask reactor provided with a reflux condenser. A 200 mL hydrochloric acid solution of a desired concentration was added and the mixture was magnetically stirred at 400 rpm under a reflux condition for a period of time from 1 to 6 hours. The system was heated to the desired temperature (from 25°C to 103°C) using a thermostatically controlled glycerol/water bath. The obtained slurry was filtered off using a vacuum Buchner filtration system and the residue was washed with 1% HCl and the wash liquor was mixed with the first filtrate. Ilmenite leachant rich in titanium and iron was produced.

The percent of titanium or iron extraction was calculated by the following formula:

$$E\% = \left(\frac{V \cdot C}{G \cdot P} \right) \cdot 100$$

where E% is the Ti or Fe extraction, %, C

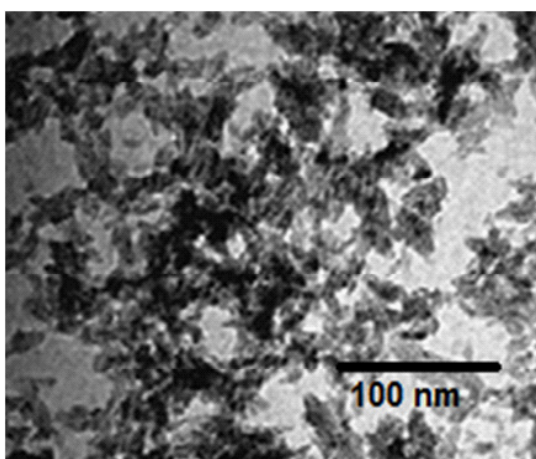


Fig. 1: TEM image of nanotitania (x 10000) magnifications

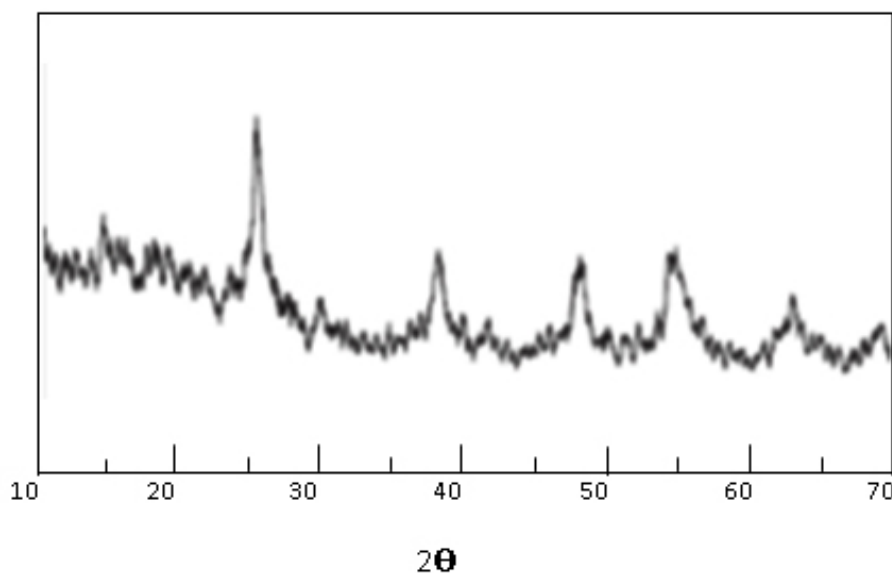


Fig. 2: X-ray diffraction pattern of titanium dioxide particles hydrolyzed from ilmenite leachant

is the Ti or Fe concentration in the leachant (g/L), V is the volume of leachant (liters), G is the total mass of the ore (g) and P is the Ti or Fe concentration in the ore.

Synthesis of nZVI Loaded on Hydrated Titania Prepared from Ilmenite

A larger scale leaching experiment of the Ilmenite Ore was performed to produce sufficient amount of the solution rich in titanium and iron at the optimum leaching conditions. In this case a 200 g ilmenite was mixed with 2000 mL hydrochloric acid at the optimum conditions of time and temperature under reflux condition. Hydration of titanium was performed as follows : in a 5000 mL Pyrex glass beaker, 4000 mL distilled water was added and

heated near boiling and then 100 mL ilmenite leachant was added and stirred magnetically. Iron powder (by the ratio 0.05 g / ml ilmenite leachant) was mixed in order to reduce almost ferric ions to ferrous ions. Once this reduction was completed, the yellowish color of ferric chloro complex turned to colorless and the hydration started immediately. A white turbidity developed with time indicating the precipitation of the hydrated titanium dioxide ($\text{TiO}_2 \cdot x\text{H}_2\text{O}$). The mixture was left at 70°C for 2 hours for completion of hydration process. The produced suspension is cooled down to room temperature and the pH was adjusted to 2.0 by adding 0.1 N NaOH.

Precipitation of nZVI on hydrated titanium dioxide was performed as follows : the whole produced amount of hydrated titanium dioxide was vigorously mixed under N_2 atmosphere at ambient temperature. A 150 mL of a 0.2 M aqueous solution of NaBH_4 was added dropwise where a black precipitate of iron was immediately appeared and the suspension turned black. The slurry was filtered off using vacuum pump and the precipitated powder was washed several times with absolute ethanol and then dried at 80°C for 24 hours.

The ferrous iron was reduced by the borohydride through the reaction shown in Eq. (1)²²:

Table 1: Chemical composition of ilmenite concentrate

Component	Weight, %
TiO_2	41.95
Fe_2O_3 (equivalent)	53.83
SiO_2	2.18
CaO	0.06
MgO	0.83
Al_2O_3	1.07
MnO	0.27
V_2O_5	0.025

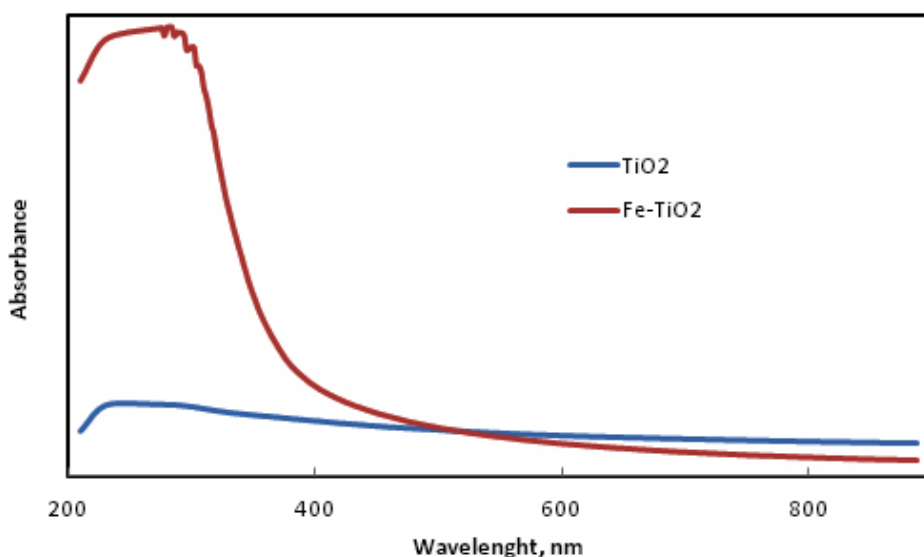
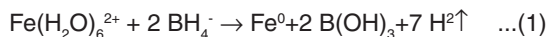


Fig. 3: UV-Vis absorbance of synthesized TiO_2 and Fe-TiO_2 and the ZVI-TiO_2



Synthesis of nZVI from Ferrous Sulfate

A 100 mL of 0.04 M aqueous solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to a three-necked flask and vigorously mixed by a mechanical stirrer fitted with a glass rod under an atmosphere of N_2 and at ambient temperature. A 100 mL of a 0.2 M aqueous solution of NaBH_4 was then added, dropwise, to the flask. The slurry was filtered off using vacuum pump and

the precipitated powder was washed several times with absolute ethanol and then dried at 80°C for 24 hours.

Nitrate Ion Reduction

Reduction of nitrate ion was studied using nZVI alone and nZVI loaded on hydrated TiO_2 . Weighed amounts of the synthesized material was added into glass vials containing 10 mL of 50 mg/L sodium nitrate ion at neutral pH and the solutions

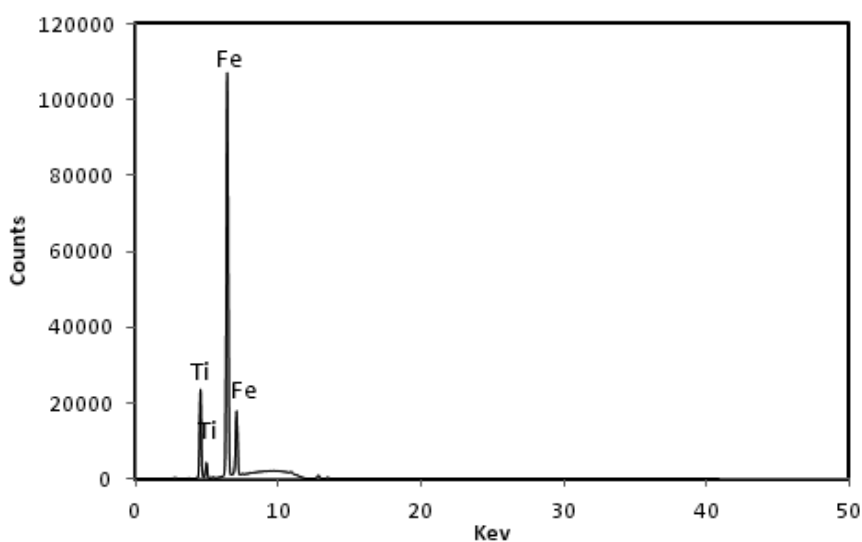


Fig. 4: EDXRF spectrum of the synthesized nZVI- TiO_2

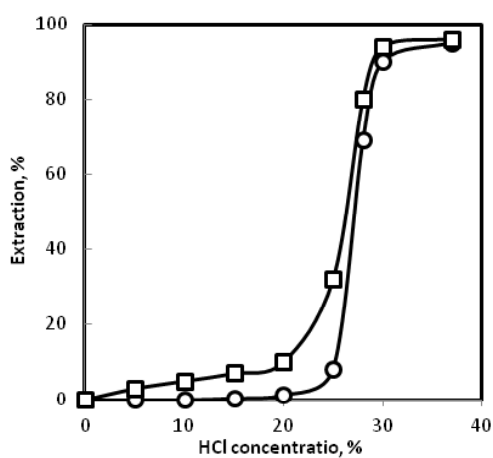


Fig. 5 : Effect of hydrochloric acid concentration on leaching of titanium and iron from ilmeniteore. (□) iron and (o) titanium

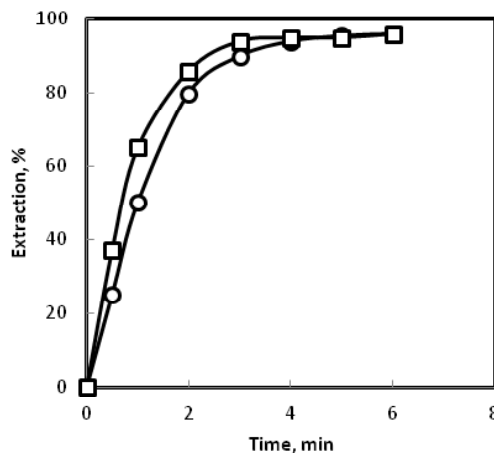


Fig. 6: Effect of time on leaching of titanium and iron from ilmeniteore. (□) iron and (o) titanium

were shaken for the required period of time at speed of 150 rpm at room temperature. After the desired time passed, the suspensions were filtered using vacuum pump and the nitrate concentrations were measured. The nitrate ion removal efficiency were calculated according to the following formula :

$$\% R = \left(\frac{C_0 - C_e}{C_0} \right) \cdot 100$$

where C_0 , C_e are the initial and the equilibrium nitrate ion concentration, respectively.

RESULTS AND DISCUSSION

Characterization of the Synthesized Materials

Characterization of the synthesized materials were investigated using TEM, XRD, UV-vis and EDXRF. TEM micrograph of nanotitania that was hydrolyzed from ilmenite ore leachant is presented in Fig. 1. Inspecting these micrographs revealed the formation of distinct leaf-like morphology nanocrystals with average diameter of 20 nm. It is possible to see the 'leafy' morphology. These 'leaves' dispersing evenly in solution so that it is stable more than 6 months at room temperature²³. The

particles looked dispersed homogeneously without agglomeration.

The X-ray diffraction pattern of titanium dioxide particles prepared by hydrolysis of the ilmenite leachant at 100 °C without any further heat

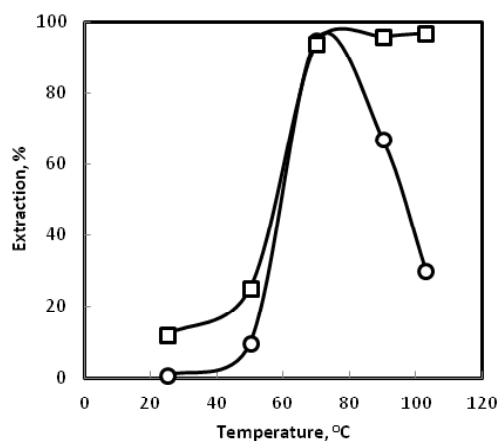


Fig. 7: Effect of temperature on leaching of titanium and iron from ilmenite ore. (□) iron and (o) titanium

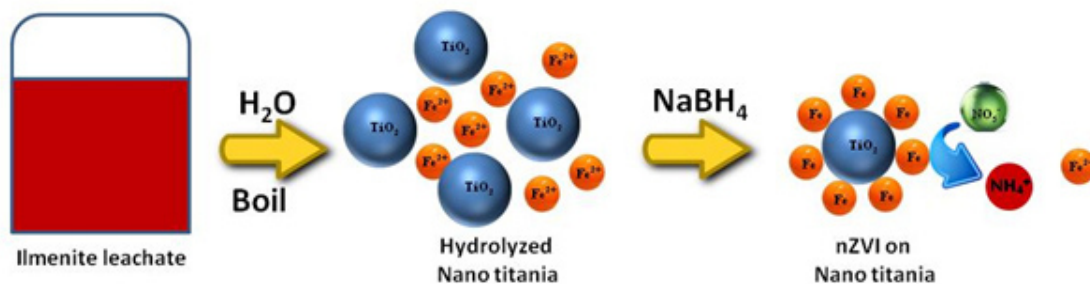


Fig. 8: Schematic diagram of synthesis of nZVI loaded TiO_2 and nitrate ion reduction

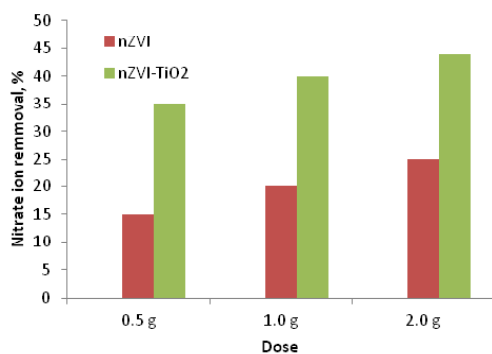


Fig. 9: Nitrate ion reduction by nZVI and nZVI- TiO_2 at pH 7 for 3 hours

treatment is shown in Fig. 2. Only anatase phase TiO_2 was detected as the main hydrolysis product. This results agrees well with our previous work where a purified $TiOCl_2$ is hydrolyzed at similar conditions²³.

The UV-Vis optical absorption of the hydrolyzed titania and nZVI loaded titania are presented in Fig. 3. The hydrolyzed titania showed sharp absorption band towards the UV region (<400 nm). However, this absorption band was absent after loading the titania with nZVI. This may be due to the adhesion of nano iron particles on titania

surface making isolating layers those are blocking any interaction of the light beams with TiO₂ surface. This may suggest that nZVI-titania particles will chemically react with the targeted nitrate ions without any catalytic or photocatalytic effect of the TiO₂ support.

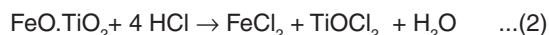
The synthesized nZVI-TiO₂ was investigated using EDXRF. Figure 4 showed that the synthesized material contains about 40 % Fe and 10 % Ti.

Studying Leaching Conditions of Ilmenite Ore

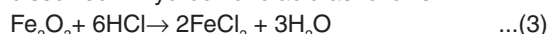
Natural ilmenite is an inexpensive raw material contains varieties of components. The major ones are TiO₂ and iron oxides. Table 1 shows an example of the chemical composition of an Egyptian low grade ilmenite ore that is used in this work. It contains a low content of TiO₂ of about 42%, and a high content of total Fe of about 38%. Though, it is considered as a low grade ilmenite ore. The extraction procedures aims at maximum dissolution of titanium and iron contents in the leachant. The rich leachant will be then utilized as a source for

synthesis of nZVI loaded on titanium dioxide.

It is known that the main minerals in ilmenite ore are ilmenite (FeTiO₃ or FeO.TiO₂) which contain iron in the divalent state and titanium in the tetravalent state, and hematite (Fe₂O₃) which contain iron in the trivalent state¹³. The ilmenite fraction in the ore is dissolved in hydrochloric acid as follows:



and the hematite fraction in the ore is dissolved in hydrochloric acid as follows:



Thus, the resulting leachant would contain Fe²⁺, Fe³⁺ and Ti⁴⁺ ions together with some metallic impurities (such as Ca²⁺, Mg²⁺, Al³⁺, Mn²⁺ and V⁵⁺) in the chloride forms and residual HCl. The following study will be concerned with optimizing the effects of HCl concentration, leaching time, and temperature for maximum extraction of titanium and iron from ilmenite ore.

Table 2: Equilibrium constants for redox half-cell reactions of nitrate ion⁴⁹

Reaction	Log K	pe ⁰	E _H ⁰ , V
NO ₃ ⁻ + 2e ⁻ + 2H ⁺ ↔ NO ₂ ⁻ + H ₂ O	28.6	14.3	0.843
NO ₃ ⁻ + 3e ⁻ + 4H ⁺ ↔ NO _(g) + 2H ₂ O	48.4	16.1	0.952
2NO ₃ ⁻ + 10e ⁻ + 12H ⁺ ↔ N _{2(g)} + 6H ₂ O	210.3	21.0	1.241
NO ₃ ⁻ + 8e ⁻ + 10H ⁺ ↔ NH ₄ ⁺ + 3H ₂ O	119.1	14.9	0.878
NO ₂ ⁻ + 6e ⁻ + 8H ⁺ ↔ NH ₄ ⁺ + 2H ₂ O	-	15.0	0.890

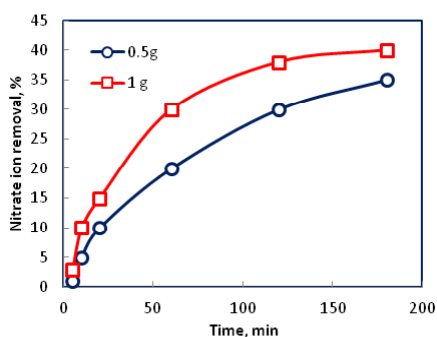


Fig. 10: Effect of shaking time on reduction of nitrate ion with nZVI-TiO₂ at pH 7

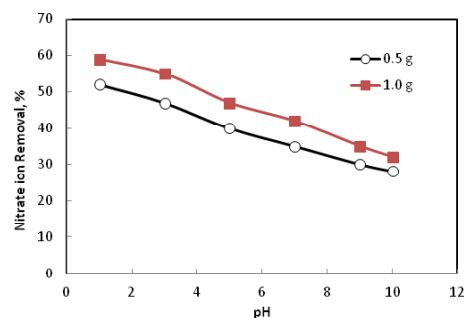


Fig. 11: Effect of pH and nZVI-TiO₂ mass on reduction of nitrate ion after 3 hours

Effect of Hydrochloric Acid Concentration

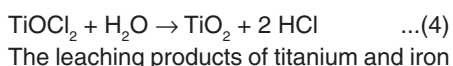
Figure 5 shows the effect of hydrochloric acid concentration on extraction percentage of titanium and iron from ilmenite ore at 70°C for 3 hours. It can be seen from this figure that hydrochloric acid was ineffective for leaching at and less than 20% where the extraction efficiencies of both metals were as low as 12% and 2% for Fe and Ti, respectively. However a sharp increase in extraction was observed at higher acid concentrations. About 94% and 90% of Fe and Ti were extracted in 30% HCl, respectively, and these values very little increased in concentrated HCl. Further studies were performed using 30% HCl.

Effect of Leaching Time

Figure 6 shows the effect of leaching time on extraction percentage of titanium and iron from ilmenite ore at 30% hydrochloric acid and 70°C. It can be seen from this figure that the extraction efficiencies continuously increased with time for both metal ions up to 3 hours and the extraction was very slightly increased at longer time. About 94% and 90% of Fe and Ti, were extracted at 3 hours, respectively. These values were increased to almost 96% after 5 hours of leaching time. The next experiments were carried out at 30% HCl for 3 hours.

Effect of Leaching Temperature

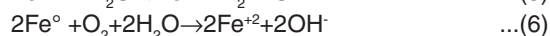
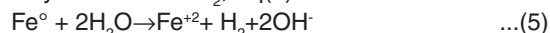
Figure 7 shows the effect of leaching temperature on extraction percentage of titanium and iron from ilmenite ore at 30% hydrochloric acid for 5 hours. It can be seen from this figure that the temperature up to 50°C was ineffective for the leaching where the extraction efficiencies were as low as 25% and 9.5% for Fe and Ti, respectively. However a sharp increase in extraction (about 95%) of both metal ions was observed at higher temperature such as 70°C. Extraction of iron was maintained at high values at higher leaching temperatures than 70°C, such as 90°C and 103°C but that of titanium continuously decreased reaching the value of 30% at 103°C. This behavior was accompanied by developing a white precipitate of probably hydrated titanium dioxide. Thus the decrease in titanium content in solution was attributed to the hydrolysis reaction of the dissolved titanyl ion (TiO^{2+}) yielding a solid TiO_2 product as follows :



from ilmenite ore are ferric chloride (FeCl_3), ferrous chloride (FeCl_2) and titanyl chloride (TiOCl_2). The hydrolysis of the latter to TiO_2 is known to be favored at low acidity and high temperature. This is consistent with our previous work²³. It is worth mentioning that at this stage the hydrolysis reaction is not favored since the main aim is to dissolve both metals. Thus, keeping the leaching temperature at 70°C is essential to avoid hydrolysis reaction. Any hydrolyzed products will be separated with residue by filtration and will be lost values of titanium.

Application Of the Synthesized nZVI-TiO₂ in Reduction of Nitrate ion Mechanism of Denitrification by nanoscale nZVI and nZVI-TiO₂

In acidic aqueous systems, zero-valent iron is easily oxidized to ferrous ion where the H^+ acts as an electron acceptor²⁴. The overall process of corrosion in anaerobic $\text{Fe}^0\text{-H}_2\text{O}$ neutral system is described by the following reaction, Eq(5). But Under aerobic conditions dissolved oxygen would play a role of the electron acceptor in the cathodic half-reaction. In this case, the primary reaction yields only OH^- and not H_2 , Eq(6):



In considering the reaction products of nitrate ion reduction, Table 2 lists possible species such as NO_2^- , NO , N_2 and NH_4^+ which depend primarily on the redox value (E_n^0). In view of redox value, the N_2 is relatively more difficult to produce ($E_n^0 = 1.241 \text{ V}$), and the next one is NO ($E_n^0 = 0.952 \text{ V}$). Though the NO_2^- might occur as one of the reaction products ($E_n^0 = 0.843 \text{ V}$), it easily becomes converted into NH_4^+ ($E_n^0 = 0.89 \text{ V}$). It appears that NH_4^+ might dominate among these reaction products. As discussed later, the end reduction product was accounted for mostly by NH_4^+ .

A schematic diagram in Fig. 8 shows the possible nitrate ion reduction mechanism. ilmenite leachant is rich in both titanium in the tetravalent state (TiO^{2+}) and iron in both divalent (Fe^{2+}) and trivalent (Fe^{3+}) states. All these species would be in the chloride forms. It is important to note that no hydration of the TiO^{2+} to the TiO_2 species will take place unless all the iron is in the Fe^{2+} state. Therefore, addition of the calculated amount of iron powder

reduces the Fe^{3+} portion to the Fe^{2+} state. At this stage the (TiO^{2+}) species can be easily converted to the white hydrated titania (TiO_2) by adding the reduced leachant to boiling water with the desired volume ratio. The pH of the suspension is then adjusted to around 2 to avoid the re-oxidation of iron. Then, the whole Fe^{2+} in the suspension is reduced to the zero valent state by addition of calculated amount of NaBH_4 . The precipitated iron sticks to the hydrated TiO_2 and the color is changed to black. The formed nZVI- TiO_2 held in suspension for about 2 hours without settling. This product is very active so that if does not separated from the solution it react with water forming the brownish $\text{Fe}(\text{OH})_3$. To avoid this, the nZVI- TiO_2 is quickly separated and thoroughly washed with ethanol and dried. When nZVI- TiO_2 is contacted with NO_3^- in water, it will reduce it mostly to NH_4^+ .

Effect of Reducing Material (nZVI or nZVI- TiO_2)

Nitrate ion reduction was firstly tested using either nZVI or nZVI loaded on TiO_2 surface (nZVI- TiO_2). Fig. 9 shows a bar graph comparing the nitrate ion reduction using 0.5g, 1.0g and 2g of each material at pH 7 for 3 hours. It can be seen that the efficiency of nZVI- TiO_2 is always superior to that of nZVI.

Effect of Shaking Time

The effect of shaking time on reduction of nitrate ion using 0.5 and 1 g nZVI- TiO_2 at pH 7 is shown in Fig 10. For the two doses, the removal efficiency % of nitrate ion continuously increased with time till about 120 min and then slowly increased. These values reached around 35% and 40% after 180 min for 0.5 and 1.0 g nZVI- TiO_2 , respectively.

Effect of Solution pH

The effect of solution pH ranging from 1 to 7 on the removal efficiency of nitrate ion after 3 hours was performed using two doses of nZVI- TiO_2 (0.5g and 1.0g) and the results were presented in Fig. 11. The results revealed that the nitrate ion removal efficiency was gradually decreasing with pH in the acidic and alkaline region. About 50% and 60% of nitrate ion could be removed at pH = 1 and these values decreased to 30% and 35% at pH = 9 using 0.5g and 1.0 g nZVI- TiO_2 doses, respectively. It is worth mentioning that the performance of Fe(0) system in terms of iron reactivity and permeability of Fe(0) bed is negatively affected at above-neutral medium as passivating minerals such as iron oxides, iron sulfides, and carbonate minerals begin to develop on Fe(0) surface.

CONCLUSION

In this work, we have succeeded in preparation of a new material composed of hydrated titanium dioxide (TiO_2) loaded with nano-zero valent iron, was successfully prepared from the inexpensive Egyptian ilmenite ore. The ilmenite ore was found suitable for leaching with hydrochloric acid to produce a solution rich in both titanium and iron ions for further processing, Using 30% hydrochloric acid at 70°C and 5 hours, most of iron and titanium in the ilmenite ore were dissolved. Nano hydrated titania was firstly produced by hydrolysis of the ilmenite leachant and nZVI was subsequently precipitated on its surface by reduction with sodium borohydride in nitrogen atmosphere. The synthesized nZVI- TiO_2 showed better performance in nitrate reduction than the nZVI alone, where the latter is easily agglomerates and its activity decreases.

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